

FUEL HOSE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a fuel hose for use in a fuel transport piping system for transporting a fuel such as gasoline, alcohol-containing gasoline (gasohol), alcohol, hydrogen, liquefied petroleum gas (LPG), compressed natural gas (CNG), light oil or dimethyl ether.

Description of the Art

With more stringent regulations against vapor emission of automotive fuels in recent years, there has been a demand for drastic reduction of the fuel vapor emission from fuel hoses. To cope with this, various types of low-permeability automotive fuel hoses have been under consideration. Examples of such fuel hoses hitherto proposed include hoses produced by employing low-permeability materials of polyester resins such as polybutylene naphthalate (PBN) and polybutylene terephthalate (PBT) which are less permeable to the fuels. However, a hose having a single layer composed of a polyester resin (PBN or PBT) alone has low flexibility, because the polyester resin is highly rigid. Therefore, it is a common practice to provide a laminate structure

including a polyester layer having a reduced thickness and a thermoplastic resin layer.

However, the polyester resins such as PBN and PBT are less adhesive to other types of materials. Therefore, the polyester resin layer and the thermoplastic resin layer are typically laminated by providing an adhesive layer therebetween. This correspondingly complicates the production process. To cope with this, there has been proposed a hose which includes an outer layer of the polyester resin such as PBN or PBT and an inner layer of a polyester thermoplastic elastomer provided on the inner periphery of the polyester resin outer layer (see, for example, Japanese Unexamined Patent Publication No. 2002-213655). The inner layer of the polyester thermoplastic elastomer and the outer layer of the polyester resin (PBN or PBT) provided on the outer periphery of the inner layer are both based on the same polyester series. Therefore, the inner layer and the outer layer can be formed by co-extrusion, and laminated and bonded without the use of an adhesive. As a result of further studies on the hose described in the aforesaid patent publication, the inventors of the present invention have found that the hose is insufficient in resistance to sour gasoline which is the result of oxidation of gasoline (sour gasoline

resistance being particularly important in applications to fuels), because the polyester thermoplastic elastomer for the inner layer is prepared by copolymerization of a large amount of a polyether component such as polytetramethylene glycol (PTMG).

In view of the foregoing, it is an object of the present invention to provide a fuel hose which is less permeable to automotive fuels and excellent in sour gasoline resistance.

SUMMARY OF THE INVENTION

To achieve the aforesaid object, a fuel hose according to the present invention comprises at least one constituent layer including an inner layer, at least the inner layer comprising a polyester resin and particles each having a core-shell structure, the particles being present in a proportion of 5 to 60 parts by weight based on 100 parts by weight of the polyester resin.

The inventors of the present invention have conducted intensive studies to provide a fuel hose which is less permeable to automotive fuels and excellent in sour gasoline resistance. As a result, the inventors have found that a fuel hose which includes at least an inner layer composed of a material prepared by blending a predetermined proportion of particles of a core-shell

structure in a polyester resin is less permeable to the fuels, excellent in sour gasoline resistance and has low-temperature flexibility. Thus, the present invention has been attained.

BRIEF DESCRIPTION OF THE DRAWING

The sole figure of the drawing is a diagram illustrating an exemplary fuel hose according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the present invention will hereinafter be described in detail.

A fuel hose according to the present invention includes an inner layer 1, an intermediate layer 2 provided on the outer periphery of the inner layer 1, and an outer layer 3 provided on the outer periphery of the intermediate layer 2 as shown in Figure. A notable feature of the present invention is that the inner layer 1 is composed of a material prepared by blending a predetermined proportion of particles of a core-shell structure in a polyester resin.

The material for the inner layer 1 contains the polyester resin and the particles of the core-shell structure.

The polyester resin to be employed is not particularly limited, but examples thereof include

polyester resin materials such as polybutylene terephthalate (PBT), polybutylene naphthalate (PBN), polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), which are used either alone or in combination.

The PBT may be prepared, for example, by a DMT method employing dimethyl terephthalate (DMT) and 1,4-butanediol, or by a direct polymerization method employing terephthalic acid (TPA) and 1,4-butanediol.

The PBN may be prepared, for example, by an ester exchange method employing 2,6-dimethyl naphthalate (DMN) and 1,4-butanediol, or by a direct polymerization method employing 2,6-naphthalenedicarboxylic acid and 1,4-butanediol.

The PEN may be prepared, for example, by an ester exchange method employing 2,6-dimethyl naphthalate (DMN) and ethylene glycol, or by a direct polymerization method employing 2,6-naphthalenedicarboxylic acid and ethylene glycol.

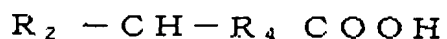
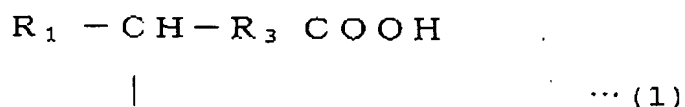
The PET may be prepared, for example, by a DMT method employing dimethyl terephthalate (DMT) and ethylene glycol, or by a direct polymerization method employing terephthalic acid (TPA) and ethylene glycol.

The polyester resin may be used in the form of a thermoplastic elastomer (TPEE) prepared by

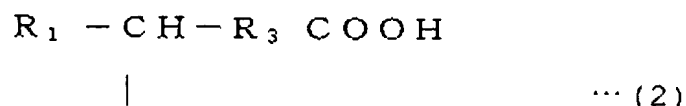
copolymerizing any of the aforesaid polyester resin materials (e.g., PBT) with at least one of a dimer acid, polycaprolactone and polytetramethylene glycol (PTMG). Further, the polyester resin may be used in the form of a blend prepared by mixing any of the aforesaid polyester resin materials (e.g., PBT) with an elastomer component. Examples of the elastomer component include olefin elastomers such as ethylene-propylene rubbers (EPM, EPDM), maleic acid modified EPMs, maleic acid modified EPDMs and olefin thermoplastic elastomers, polyester thermoplastic elastomers, polyamide thermoplastic elastomers, styrene thermoplastic elastomers, polyurethane thermoplastic elastomers, butadiene rubbers, acrylonitrile-butadiene rubbers (NBR), hydrogenated NBRs, styrene-butadiene rubbers (SBR), hydrogenated SBRs, isoprene rubbers, fluorinated rubbers, acryl rubbers, ethylene-ethyl acrylate copolymers (EEA) and ethylene-glycidyl methacrylate copolymers (EGMA), which may be used either alone or in combination.

The dimer acid is a dimer obtained through a reaction of two molecules of an organic acid. Examples of the dimer acid include aliphatic dimer acids, alicyclic dimer acids and aromatic dimer acids, which may be used either alone or in combination.

Examples of the aliphatic dimer acids include dimer acids represented by the following general formulae (1) and (2). These dimer acids may be used either alone or in combination.

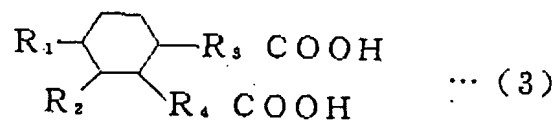


wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 and R_4 are the same or different, each representing an alkylene group; and R_1 to R_4 preferably have a total carbon number of 24 to 36.

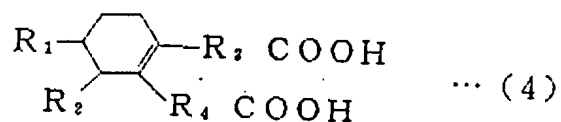


wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 represents an alkylene group; and R_1 to R_3 preferably have a total carbon number of 24 to 36.

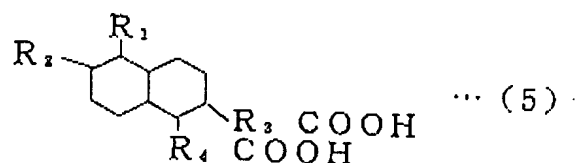
Examples of the alicyclic dimer acids include dimer acids represented by the following general formulae (3), (4), (5) and (6). These dimer acids may be used either alone or in combination.



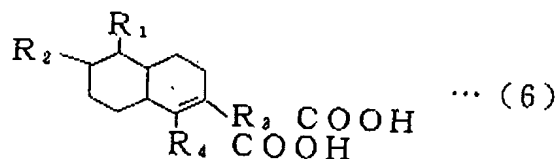
wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 and R_4 are the same or different, each representing an alkylene group; and R_1 to R_4 preferably have a total carbon number of 24 to 36.



wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 and R_4 are the same or different, each representing an alkylene group; and R_1 to R_4 preferably have a total carbon number of 24 to 36.

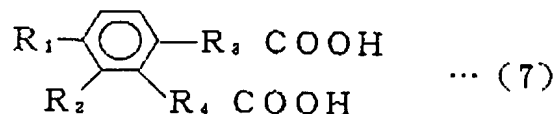


wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 and R_4 are the same or different, each representing an alkylene group; and R_1 to R_4 preferably have a total carbon number of 24 to 36.



wherein R_1 and R_2 are the same or different, each representing an alkyl group; R_3 and R_4 are the same or different, each representing an alkylene group; and R_1 to R_4 preferably have a total carbon number of 24 to 36.

Examples of the aromatic dimer acids include dimer acids represented by the following general formula (7).



wherein R₁ and R₂ are the same or different, each representing an alkyl group; R₃ and R₄ are the same or different, each representing an alkylene group; and R₁ to R₄ preferably have a total carbon number of 24 to 36.

Specific preferred examples of the dimer acids include PRIPOL 1008 (a hydrogenated dimer acid having a carbon number of 36 and containing aromatic, alicyclic and aliphatic dimer acids in a molar ratio of 9/54/37) available from Uniqema of Gouda, the Netherlands, PRIPOL 1009 (a hydrogenated dimer acid having a carbon number of 36 and containing aromatic, alicyclic and aliphatic dimer acids in a molar ratio of 13/64/23) available from Uniqema of Gouda, the Netherlands, PRIPOL 1098 (a non-hydrogenated dimer acid having a carbon number of 36 and containing aromatic, alicyclic and aliphatic dimer acids in a molar ratio of 13/64/23) available from Uniqema of Gouda, the Netherlands, PRIPLAST 3008 (containing dimethyl esters of the dimer acids of PRIPOL 1008) available from Uniqema of Gouda, the Netherlands, and PRIPLAST 1899 (containing dimethyl esters of the

dimer acids of PRIPOL 1009) available from Uniqema of Gouda, the Netherlands. Among these dimer acids, the hydrogenated dimer acids PRIPOL 1008, PRIPOL 1009, PRIPLAST 3008 and PRIPLAST 1899 are particularly preferred.

In the present invention, the particles of the core-shell structure (hereinafter referred to as "core-shell polymer") to be used in combination with the polyester resin are not particularly limited. For example, the core-shell polymer may have a multi-layer structure including a core of a rubber polymer and a shell layer of a glassy polymer. The core and the shell layer are generally combined by graft copolymerization.

The rubber polymer for the core is not particularly limited. From the viewpoint of the impact resistance, it is preferred that the rubber polymer has a glass transition temperature (T_g) of not higher than -10°C , more preferably not higher than -30°C .

Examples of the rubber polymer for the core include a silicon containing elastomer, a diene elastomer and an acryl elastomer, which may be used either alone or in combination.

The silicon containing elastomer is prepared, for example, by polymerization of an organosiloxane monomer. Examples of the organosiloxane monomer include

hexamethyltricyclosiloxane, octamethylcyclosiloxane, decamethylpentacyclosiloxane, dodecamethylhexacyclosiloxane, trimethyltriphenylsiloxane, tetramethylphenylcyclotetrasiloxane and octaphenylcyclotetrasiloxane, which may be used either alone or in combination.

An example of the diene elastomer is polybutadiene prepared by polymerization of a butadiene monomer.

The acryl elastomer is prepared, for example, by polymerization of an acrylate and a small amount of a cross-linking monomer. Examples of the acrylate include butyl acrylate, methyl acrylate, ethyl acrylate, propyl acrylate, hexyl acrylate and 2-ethylhexyl acrylate, which may be used either alone or in combination. Examples of the cross-linking monomer include esters, such as butylene diacrylate and butylene dimethacrylate, of acrylic acid and polyols (e.g., trimethylolpropane), vinyl compounds such as divinylbenzene, vinyl acrylate and vinyl methacrylate, and allyl compounds such as allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate, diallyl itaconate, monoallyl maleate, monoallyl fumarate, triallyl cyanurate, which may be used either alone or in combination.

From the viewpoint of impact resistance, it is preferred that the rubber polymer for the core is present in a proportion of 50 to 90 wt% in the core-shell polymer.

The glassy polymer for the shell layer is not particularly limited. For the ease of handling, the glassy polymer preferably has a T_g of not lower than 30° C, more preferably not lower than 40° C.

Examples of the glassy polymer for the shell layer include vinyl polymers. The vinyl polymers may be prepared by polymerization or copolymerization of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers, methacrylate monomers and acrylate monomers.

To improve the compatibility with the polyester resin and the improvement of the impact resistance, the glassy polymer for the shell layer preferably has a polar functional group in its molecule. The polar functional group is not particularly limited, but examples thereof include a carboxyl group, an ester group, an amide group, an epoxy group, an amino group, a hydroxyl group and an ether group, among which the epoxy group and the carboxyl group are particularly preferred for the improvement of the impact resistance.

The core-shell polymer preferably has an average particle diameter of 50 to 1000nm, particularly

preferably 100 to 700nm. The core and the shell layer may each have a multi-layer structure including two or more sublayers.

Specific examples of the core-shell polymer include a core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) including a shell layer composed of a glassy polymer having epoxy groups, and a core-shell polymer (IM-301 available from Ganz Chemical Co., Ltd.) including a shell layer composed of a glassy polymer having carboxyl groups.

In the present invention, the core-shell polymer preferably should be present in a proportion of 5 to 60 parts by weight (hereinafter referred to simply as "parts"), more preferably 10 to 40 parts, based on 100 parts of the polyester resin. If the proportion of the core-shell polymer is smaller than 5 parts, the impact resistance may not be improved, and the low-temperature flexibility may deteriorate. If the proportion of the core-shell polymer is greater than 60 parts, the thermal aging resistance tends to deteriorate, and the fuel hose tends to be greatly swelled by gasoline.

The inner layer 1 (see the Figure) described above may be imparted with electrical conductivity by blending an electrically conductive material such as carbon black, carbon nanotube and metal powder in the inner layer

material so as to release static electricity, generated by a fuel pump, from the hose to outside the hose to prevent ignition of a fuel (such as gasoline) and a like accident which may otherwise occur due to the static electricity.

The material for the intermediate layer 2 provided on the outer periphery of the inner layer 1 is not particularly limited, but preferred examples thereof include polyester resins such as PBT, PBN, PET and PEN. The polyester resin may be used in the form of a thermoplastic elastomer (TPEE) or a blend with an elastomer component as described above. The intermediate layer material may contain the aforesaid core-shell polymer in addition to the polyester resin.

Like the inner layer 1, the intermediate layer 2 may be imparted with electrical conductivity by blending an electrically conductive material such as carbon black, carbon nanotube or metal powder in the intermediate layer material.

The material for the outer layer 3 provided on the outer periphery of the intermediate layer 2 may be, for example, a thermoplastic elastomer (TPEE) or a blend of a polyester resin and an elastomer component. The outer layer material may further contain the aforesaid core-shell polymer.

A polyamide or an amine-rich resin may be employed as the outer layer material. The use of the polyamide or the amine-rich resin as the outer layer material is advantageous for improving the flexibility of the hose. The amine-rich resin herein means a resin having an amine group content of not smaller than about 4×10^{-5} g-equivalents/g. Further, the use of the amine-rich resin is advantageous for improving the adhesiveness. An ordinary polyamide not enriched with amine has an amino group content of about 3×10^{-5} g-equivalents/g, which is lower than that of the amine-rich resin employed in the present invention. The amino group content is determined, for example, by a neutralization potentiometric titration method.

The amine-rich resin will be described in greater detail. The amine-rich resin is prepared, for example, by mixing or reacting a compound containing amino groups with a thermoplastic resin. The thermoplastic resin may be a polyamide or a polyolefin. The polyamide is more preferable in terms of heat resistance, fuel/oil resistance and mechanical strength. Specific examples of the polyamide include PA6, PA610, PA612, PA99, PA912, PA6/66 copolymers, PA11 and PA12, among which PA11 and PA12 are particularly preferred. Examples of the polyolefin include polyethylene, polypropylene,

polybutene, ethylene-propylene copolymers and olefin thermoplastic elastomers, which may be used either alone or in combination. The amino group containing compound to be mixed or reacted with the thermoplastic resin is not particularly limited, but examples thereof include m-xylylenediamine, p-xylylenediamine, hexamethylenediamine, dodecamethylenediamine, aliphatic diamines, aliphatic polyamines, γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane and amino-modified resins.

Where the polyamide is employed as the thermoplastic resin, the amine-rich resin is prepared by melt-mixing the amino group containing compound with the polyamide, or by modifying carboxyl groups of the polyamide with amino groups after polymerization (e.g., by bonding a diamine compound to terminal carboxyl groups). Where the polyolefin such as polyethylene, polypropylene, polybutene, an ethylene-propylene copolymer or an olefin thermoplastic elastomer is employed as the thermoplastic resin, the amine-rich resin is prepared in the same manner as described above by the addition of amino groups.

Like the inner layer 1, the outer layer 3 may be imparted with electrical conductivity by blending an electrically conductive material such as carbon black,

carbon nanotube or metal powder in the outer layer material.

The inventive fuel hose is produced, for example, in the following manner. The inner layer material essentially containing the polyester resin and the core-shell polymer, the intermediate layer material and the outer layer material are prepared. Then, these materials are co-extruded by means of an extruder, and the resulting inner, intermediate and outer layers are sized by way of vacuum sizing and cooled to solidification in a cooling water bath. Thus, the intended fuel hose (see the Figure) is produced. The inventive fuel hose may at least partly have a bellow structure, which is created, for example, by a corrugator.

In the aforesaid production process, the inner layer 1, the intermediate layer 2 and the outer layer 3 are formed by the co-extrusion method. However, the method for the formation of the inner, intermediate and outer layers is not limited to the co-extrusion method. For example, the inner layer 1 may first be formed by extrusion, and then the intermediate and outer layers 2, 3 may sequentially be formed on the outer periphery of the inner layer 1 by extrusion.

The inner layer 1 of the inventive fuel hose

typically has a thickness of 0.01 to 1 mm, preferably 0.05 to 0.4 mm. The intermediate layer 2 typically has a thickness of 0.01 to 0.5 mm, preferably 0.05 to 0.4 mm. The outer layer 3 typically has a thickness of 0.1 to 3 mm, preferably 0.3 to 1 mm. The inventive fuel hose typically has an inner diameter of 3 to 60 mm, preferably 4 to 30 mm.

The structure of the inventive fuel hose is not limited to the three-layer structure shown in the Figure, but may have a single-layer structure, a two-layer structure or a multi-layer structure having four or more layers. However, at least the inner layer of the fuel hose (the hose itself if the hose has a single-layer structure) should be composed of the material containing the polyester resin and the predetermined proportion of the core-shell polymer.

Where the polyamide described above is employed as the outer layer material, an adhesive layer is preferably provided between the polyamide outer layer and a layer inwardly adjacent to the outer layer. An adhesive for the adhesive layer is prepared, for example, by mixing PBT and PA 12 in a weight ratio of 50:50 and kneading the resulting mixture by means of a twin screw extruder.

Where the amine-rich resin described above is

employed as the outer layer material, mating surfaces of the amine-rich resin outer layer and a layer inwardly adjacent to the outer layer are preferably subjected to a plasma treatment. The plasma treatment of the layer inwardly adjacent to the amine-rich resin outer layer makes it possible to bond these layers without the use of an adhesive and, therefore, is advantageous in terms of operability. The conditions for the plasma treatment are not particularly limited, but the plasma treatment is typically performed at a frequency of 0.1 to 1000 MHz, preferably 1 to 100 MHz, at a high frequency power output of 2 to 300 W, preferably 5 to 200 W, for a treatment period of 2 to 180 seconds, preferably 5 to 60 seconds.

The inventive fuel hose is advantageously employed as a hose for a vehicle such as an automobile. Further, the fuel hose may be employed for agricultural vehicles such as tractors and cultivators.

Next, an explanation will be given to Examples of the present invention and Comparative Examples.

Prior to the explanation of Examples and Comparative Examples, materials herein employed will be explained.

PBN

TQB-OT available from Teijin Chemicals, Ltd.

PBT

CELANEX 2001 available from Polyplastics Co., Ltd.

Non-conductive PBT + core shell (1)

A material prepared by mixing 10 parts of a core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) having a shell layer of a glassy polymer having epoxy groups with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (2)

A material prepared by mixing 20 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (3)

A material prepared by mixing 10 parts of a core-shell polymer (IM-301 available from Ganz Chemical Co., Ltd.) having a shell layer of a glassy polymer having carboxyl groups with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (4)

A material prepared by mixing 2 parts of the aforesaid core-shell polymer (IM-301 available from Ganz Chemical Co., Ltd.) with 100 parts of PBT (CELANEX 2001 available

from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (5)

A material prepared by mixing 5 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (6)

A material prepared by mixing 60 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Non-conductive PBT + core shell (7)

A material prepared by mixing 100 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) with 100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Conductive PBT + core shell

A material prepared by mixing 10 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) and 4 parts of carbon black (KETJEN BLACK EC600JD available from Ketjen Black Internal Co.) with

100 parts of PBT (CELANEX 2001 available from Polyplastics Co., Ltd.) and kneading the resulting mixture by means of a twin screw extruder.

Conductive PBT-dimer + core shell

A material prepared by mixing 10 parts of the aforesaid core-shell polymer (IM-203 available from Ganz Chemical Co., Ltd.) and 4 parts of carbon black (KETJEN BLACK EC600JD available from Ketjen Black Internal Co.) with 100 parts of PBT-TPEE (PBTS01562 available from Kanebo Gosen Co., Ltd. and having a dimer acid content of 6 mol%) and kneading the resulting mixture by means of a twin screw extruder.

PBT blend

A blend (GRILPET B24HNZ available for EMS CHEMIE AG of Domat, Switzerland) of PBT (85 wt%) and an olefin elastomer (15 wt%).

PBT-TPEE (1)

HYTREL 5577R07 available from Toray Du Pont Co., Ltd.

PBT-TPEE (2)

PBTS01524 available from Kanebo Gohsen Co., Ltd.

PA12

AESN OP20TL available from Atofina Japan Co., Ltd.

Amine-rich PA12

BESTAMIDE LX9011 (having an amino group content of 5×10^{-5} g.equivalents/g) available from Daicel-Degussa Ltd.

By employing the materials described above, fuel hoses were produced in the following manner.

Example 1

First, an inner layer material as shown in Table 1 was prepared. The inner layer material was extruded by means of an extruder, and then cooled to solidification in a cooling water bath. Thus, a fuel hose of a single-layer structure (having an inner diameter of 6 mm and an outer diameter of 8 mm) was produced.

Example 2

First, an inner layer material and an outer layer material as shown in Table 1 were prepared. The inner layer material and the outer layer material were co-extruded by means of an extruder, and then cooled to solidification in a cooling water bath. Thus, a fuel hose of a two-layer structure (having an inner diameter of 6 mm and an outer diameter of 8 mm) was produced, which included an inner layer and an outer layer provided on the outer periphery of the inner layer.

Example 3

First, an inner layer material, a material for an intermediate layer A and an outer layer material as shown in Table 1 were prepared. The inner layer material, the material for the intermediate layer A and the outer layer

material were co-extruded by means of an extruder, and then cooled to solidification in a cooling water bath. Thus, a fuel hose of a three-layer structure (having an inner diameter of 6 mm and an outer diameter of 8 mm) was produced, which included an inner layer, an intermediate layer A provided on the outer periphery of the inner layer and an outer layer provided on the outer periphery of the intermediate layer A.

Examples 4 to 15, 17, 19, 21 to 25 and Comparative Examples 1 to 5

Inner layer materials, intermediate layer materials and outer layer materials as shown in Tables 1 to 5 were prepared. By employing these materials, fuel hoses of a two-layer structure, a three-layer structure, a four-layer structure and a five-layer structure (having an inner diameter of 6 mm and an outer diameter of 8 mm) were produced in substantially the same manner as in Examples 2 and 3.

Example 16

First, an inner layer material and an outer layer material as shown in Table 3 were prepared. The inner layer material was extruded by means of an extruder for formation of an inner layer. Then, the inner layer was introduced between electrodes in a discharge chamber of a reduced pressure plasma treatment apparatus (employing

Ar as a discharge gas at a pressure of 0.1 Torr). High-frequency power having an impedance-matched frequency of 13.56 MHz and an output of 10 W was applied to the electrodes by means of a high-frequency power source and a matching box to cause a glow discharge for generation of plasma. Thus, the outer peripheral surface of the inner layer was subjected to a plasma treatment. In turn, the outer layer material was extruded onto the plasma-treated surface of the inner layer by means of an extruder. Thus, a fuel hose of a two-layer structure (having an inner diameter of 6 mm and an outer diameter of 8 mm) was produced, which included an outer layer provided on the plasma-treated outer peripheral surface of the inner layer.

Examples 18 and 20

Inner layer materials, intermediate layer materials and outer layer materials as shown in Tables 3 and 4 were prepared. Then, the plasma treatment was performed in the same manner as in Example 16. Thus, fuel hoses (having an inner diameter of 6 mm and an outer diameter of 8 mm) were produced. In the tables, a layer subjected to the plasma treatment is shown in the item "Plasma treatment". For example, the notation "intermediate layer A" in the item "Plasma treatment" means that the surface of the intermediate layer A was

plasma-treated.

The fuel hoses of Examples and Comparative Examples thus produced were evaluated for characteristic properties thereof in the following manner. The results are shown in Tables 1 to 5.

Permeability to gasoline

Opposite end portions of a 10-m long fuel hose (inner diameter: 6 mm) were each expanded to an inner diameter of 10 mm by means of a cone-shaped jig. Two metal pipes each having an outer diameter of 8 mm with two bulged portions, each having an outer diameter of 10 mm, and with one end thereof having a rounded outer periphery were prepared. The metal pipes were respectively press-fitted into the opposite end portions of the hose. A blind cap was threadingly attached to one of the metal pipes, and a metal valve was attached to the other metal pipe. Thereafter, regular gasoline (containing 10 vol% ethanol) was supplied into the fuel hose through the metal pipe having the metal valve, and the fuel hose was sealed. The fuel hose was allowed to stand at 40° C for 3000 hours (the regular gasoline was replaced every week). Then, gasoline permeation was measured for three days on the basis of a Diurnal Breathing Loss (DBL) pattern by the Sealed Housing for Evaporative Detection (SHED) method in accordance with

California Air Resources Board (CARB). Then, fuel permeation per meter of the hose was determined on a day when the maximum permeation was detected. In Tables 1 to 5, the notation "<0.1" indicates that the measured fuel permeation was below the measurement limitation (0.1 mg/m/day) of the aforesaid measurement method.

Sour gasoline resistance

A model of degraded (sour) gasoline was prepared by blending 5 wt% of lauroyl peroxide (LPO) in Fuel C (50 vol% of toluene + 50 vol% isooctane). Then, two metal pipes were respectively press-fitted into opposite end portions of a 10-m long fuel hose. After the model of degraded gasoline was circulated through the fuel hose at 60 °C at a pressure of 0.3 MPa for eight hours via a pressure regulator, the model of degraded gasoline was filled in the fuel hose for 16 hours. After this cycle was repeated 30 times, a part of the fuel hose was sampled and bent by 180 degrees. The state of the sampled part was visually observed for the evaluation of the sour gasoline resistance. In Tables 1 to 5, the symbol ○ indicates that the fuel hose did not suffer from any abnormalities, and the symbol × indicates that the fuel hose folded down.

Hydrolysis resistance

After a fuel hose was allowed to stand at a

temperature of 80° C at a humidity of 95% for 1000 hours, the hose was bent by 180 degrees for the evaluation of the hydrolysis resistance. In Tables 1 to 5, the symbol × indicates that the fuel hose suffered from abnormalities such as fold-down, and the symbol ○ indicates that the hose did not suffer from any abnormalities.

Low-temperature flexibility

After a fuel hose was refrigerated at -40° C for four hours, the fuel hose was bent by 180 degrees for the evaluation of the low-temperature flexibility. In Tables 1 to 5, the symbol × indicates that the fuel hose suffered from abnormalities such as fold-down, and the symbol ○ indicates that the hose did not suffer from any abnormalities.

Table 1

	Example					
	1	2	3	4	5	6
Inner layer material	*1	*1	*1	*1	*1	*1
Material for intermediate layer A	-	-	PBT	PBT	PBT	PBT
Material for intermediate layer B	-	-	-	*1	PBT blend	TPEE(2)
Material for intermediate layer C	-	-	-	-	-	-
Outer layer material	-	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)
Thickness (μm)						
Inner layer	1000	400	300	300	300	300
Intermediate layer A	-	-	300	300	300	300
Intermediate layer B	-	-	-	200	200	200
Intermediate layer C	-	-	-	-	-	-
Outer layer	-	600	400	200	200	200
Plasma treatment	-	-	-	-	-	-
Gasoline permeability (mg/m/day)	0.8	1.8	1.2	0.8	0.9	1.2
Sour gasoline resistance	O	O	O	O	O	O
Hydrolysis resistance	O	O	O	O	O	O
Low-temperature flexibility	O	O	O	O	O	O

*1: Non-conductive PBT + core-shell (1)

Table 2

	Example					
	7	8	9	10	11	12
Inner layer material	*9	*1	*2	*3	*1	*8
Material for intermediate layer A	*1	PBN	PBN	PBN	PBN	*1
Material for intermediate layer B	PBT	-	-	-	*1	PBN
Material for intermediate layer C	*1	-	-	-	-	-
Outer layer material	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(2)	TPEE(1)
Thickness (μm)						
Inner layer	100	300	300	300	300	100
Intermediate layer A	300	100	100	100	100	200
Intermediate layer B	200	-	-	-	200	100
Intermediate layer C	200	-	-	-	-	-
Outer layer	200	600	600	600	400	600
Plasma treatment	-	-	-	-	-	-
Gasoline permeability (mg/m/day)	1.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sour gasoline resistance	○	○	○	○	○	○
Hydrolysis resistance	○	○	○	○	○	○
Low-temperature flexibility	○	○	○	○	○	○

*1: Non-conductive PBT + core-shell (1)

*2: Non-conductive PBT + core-shell (2)

*3: Non-conductive PBT + core-shell (3)

*8: Conductive PBT + core-shell

*9: Conductive PBT-dimer + core-shell

Table 3

	Example							
	13	14	15	16	17	18		
Inner layer material	*8	*8	*1	*1	*1	*1		
Material for intermediate layer A	*1	PBT blend	*11	-	PBN	PBN		
Material for intermediate layer B	PBN	PBN	-	-	*11	-		
Material for intermediate layer C	*1	PBT bland	-	-	-	-		
Outer layer material	TPEE(2)	TPEE(2)	PA12	*10	PA12	*10		
Thickness (μm)								
Inner layer	100	100	400	400	300	300		
Intermediate layer A	200	200	100	-	100	100		
Intermediate layer B	100	100	-	-	100	-		
Intermediate layer C	200	200	-	-	-	-		
Outer layer	400	400	500	600	500	600		
Plasma treatment	-	-	-	Inner layer	-	Intermediate layer A		
Gasoline permeability (mg/m/day)	<0.1	<0.1	1.7	1.6	<0.1	<0.1		
Sour gasoline resistance	O	O	O	O	O	O		
Hydrolysis resistance	O	O	O	O	O	O		
Low-temperature flexibility	O	O	O	O	O	O		

*1: Non-conductive PBT + core-shell (1) *8: Conductive PBT + core-shell

*10: Amine-rich PA12

*11: Adhesive prepared by mixing PBT with PA12 in weight ratio of 50:50 by a twin screw extruder.

Table 4

	Example							
	19	20	21	22	23	24		
Inner layer material	*8	*8	*9	*9	*9	*5		
Material for intermediate layer A	*1	*1	*1	PBT blend	*1	PBN		
Material for intermediate layer B	PBN	PBN	PBN	PBN	PBN	-		
Material for intermediate layer C	*11	-	-	PBT blend	*1	-		
Outer layer material	PA12	*10	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)		
Thickness (μm)								
Inner layer	100	100	100	100	100	300		
Intermediate layer A	200	200	200	350	350	100		
Intermediate layer B	100	100	100	100	100	-		
Intermediate layer C	100	-	-	200	200	-		
Outer layer	500	600	600	250	250	600		
Plasma treatment	-	Intermediate layer B	-	-	-	-		
Gasoline permeability (mg/m/day)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		
Sour gasoline resistance	O	O	O	O	O	O		
Hydrolysis resistance	O	O	O	O	O	O		
Low-temperature flexibility	O	O	O	O	O	O		

*1: Non-conductive PBT + core-shell (1) *5: Non-conductive PBT + core-shell (5)

*8: Conductive PBT + core-shell *9: Conductive PBT-dimer + core shell

*10: Amine-rich PA12

*11: Adhesive prepared by mixing PBT with PA12 in weight ratio of 50:50 by a twin screw extruder.

Table 5

	Example	Comparative Example				
		1	2	3	4	5
Inner layer material	25					
	*6	PBT	PBN	TPEE(1)	*4	*7
Material for intermediate layer A	PBN	-	-	PBN	PBN	PBN
Material for intermediate layer B	-	-	-	-	-	-
Material for intermediate layer C	-	-	-	-	-	-
Outer layer material	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)	TPEE(1)
Thickness (μm)						
Inner layer	300	400	400	300	300	300
Intermediate layer A	100	-	-	100	100	100
Intermediate layer B	-	-	-	-	-	-
Intermediate layer C	-	-	-	-	-	-
Outer layer	600	600	600	600	600	600
Plasma treatment	-	-	-	-	-	-
Gasoline permeability (mg/m/day)	<0.1	11.0	305	<0.1	<0.1	<0.1
Sour gasoline resistance	O	O	O	x	O	O
Hydrolysis resistance	O	x	O	O	O	O
Low-temperature flexibility	O	x	x	O	x	O
Remark	-	-	-	-	-	*12

*4: Non-conductive PBT + core-shell (4)

*6: Non-conductive PBT + core-shell (6)

*7: Non-conductive PBT + core-shell (7)

*12: Poor in resistance to thermal aging, and greatly swelled by gasoline.

As can be understood from the results shown in the Tables, the fuel hoses of the Examples were less permeable to gasoline, and were excellent in sour gasoline resistance, hydrolysis resistance and low-temperature flexibility.

On the other hand, the inner layer of the fuel hose of Comparative Example 1, which was composed of PBT, cracked over time due to strains occurring therein when the opposite end portions of the hose were expanded by the press-fitting of the metal pipes. Therefore, the fuel hose suffered from leakage of gasoline and a slightly greater gasoline permeability. Further, the fuel hose was inferior in low-temperature flexibility and hydrolysis resistance. The inner layer of the fuel hose of Comparative Example 2, which was composed of PBN, cracked over time due to strains occurring therein when the opposite end portions of the hose were expanded by the press-fitting of the metal pipes. Therefore, the fuel hose suffered from leakage of gasoline and a much greater gasoline permeability. Further, the fuel hose was inferior in low-temperature flexibility. The fuel hose of Comparative Example 3, with its inner layer composed of PBT-TPEE (1) having a higher polyether content, folded down, and was inferior in sour gasoline resistance. The fuel hose of Comparative Example 4,

with its inner layer composed of the material containing the core-shell polymer in an excessively small proportion, folded down, and was inferior in low-temperature flexibility. The fuel hose of Comparative Example 5, with its inner layer composed of the material containing the core-shell polymer in an excessively great proportion, was less resistance to thermal aging, and was greatly swelled by gasoline.

According to the present invention, at least the inner layer of the fuel hose was composed of the material prepared by blending a predetermined proportion of a core-shell polymer in a polyester resin. The fuel hose is less permeable to the fuel, and is excellent in sour gasoline resistance and low-temperature flexibility.

When at least the inner layer of the fuel hose is imparted with electrical conductivity by employing the electrically conductive material, static electricity generated by a fuel pump can be released out of the hose. Therefore, ignition of the fuel (such as gasoline) and a like accident can be prevented, which may otherwise occur due to the static electricity.

When all the constituent layers of the fuel hose are composed of the materials based on the polyester resin, the layers can be bonded to one another without the use of an adhesive. This is advantageous in terms

of operability and production.

When the outermost layer of the fuel hose comprises a polyamide, the low-temperature flexibility of the hose is improved.

When the intermediate layer comprises a second polyester resin such as PBT and an amine-rich resin layer is provided on the outer peripheral surface of the intermediate layer which has been subjected to an electric discharge treatment, the amine-rich resin layer and the intermediate layer can be bonded to each other without the use of an adhesive. This is advantageous in terms of operability and production.

When at least one intermediate layer of the fuel hose comprises a second polyester resin such as PBT, the hose is further less permeable to the fuel.

When the outermost layer of the fuel hose comprises a PBT thermoplastic elastomer, the low-temperature flexibility of the hose is further improved.

When the layers in contact with the inner and outer surfaces of the intermediate layer composed of the second polyester resin each comprise at least one of a blend of polybutylene terephthalate and an elastomer component, and a polybutylene terephthalate material containing particles each having the core-shell structure, the low-temperature flexibility of the hose is further

improved.